Tailored Nanopost Arrays for Nanophotonic Ion Production

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Proposal Title
Laser Desorption Ionization of Biomolecules from Silicon Microcolumn and Nanopost Arrays

Research Achievement
Recently we have demonstrated that quasi-periodic nanostructures with features commensurate with the wavelength of the radiation, such as laser-induced silicon microcolumn arrays (LISMA), can serve as nanophotonic ion sources for the mass spectrometry of organic and biomolecules.[1,2] In contrast to conventional laser desorption ionization, nanophotonic ion production relies on antenna-like harvesting of energy from the electromagnetic radiation by the nanostructure, confinement of the deposited energy within the nanostructure and confinement of the desorbed plume in the troughs of the surface. Recently we found a dramatic dependence of the ion yield on the polarization and incidence angle of the desorption laser beam.[2] As the LISMA periodicity is commensurate with the wavelength of the desorption laser, interference effects are also anticipated. This might be combined with local field enhancement due to near field effects. LISMA, however, can only be produced with a limited range of surface morphologies. This hinders mechanistic studies and the optimization of ion production properties.

Silicon nanopost arrays (NAPA) exhibit the essential geometrical features of LISMA and can be produced by nanofabrication with a broad range of morphologies. Tailoring the NAPA dimensions, such as post diameter, post height and periodicity, enable both studying the ion production mechanism and finding the geometry with optimum ion yield. NAPA were produced from high conductivity silicon at the Center for Nanophase Materials Sciences of the Oak Ridge National Laboratory. Initially NAPA patterns with a range of diameters (50 nm to 600 nm) and periodicities (100 nm to 1100 nm) were created with electron beam lithography. The various post heights (200 nm to 1600 nm) were achieved with deep reactive ion etching. An example of such a tailored NAPA is shown in Figure 1.

Similar to LISMA, NAPA structures also exhibited a strong orientation dependence, where the p-polarized beam produced efficient ionization in contrast to the s-polarized beam, which produced minimal or no ions. This behavior confirmed that NAPA could also be viewed as optical antenna arrays for energy deposition.

To gain insight into the energy transfer to the ions, their internal energy was probed by taking survival yield measurements (SY) at various fluences using a set of benzyl-substituted benzylpyridinium cations as thermometer ions. These studies as a function of NAPA geometries showed that NAPA with 100 nm post diameters had decreasing SYs as laser fluence was increased, whereas larger post diameters (200 nm to 500 nm) exhibited stable survival yields at low to medium fluences and increasing SYs at higher laser intensities (see Figure 2). This dramatic disparity may be attributed to the confinement of the deposited energy in the 100 nm diameter posts resulting in significantly higher surface temperatures.

Preliminary optimization studies indicated that NAPA with post diameters of 200 nm and post heights of 1200 nm resulted in the highest ionization efficiencies and that NAPA with periodicities comparable to the wavelength of irradiation produced elevated ion yields.

Future Work

NAPA are novel ion sources for mass spectrometry with high sensitivity and mass resolution. Similar to LISMA, but in contrast to other soft laser desorption ionization methods, NAPA enables fine control over ion yields and fragmentation, where intact molecular ions are observed at low laser fluences, and at higher fluences structure specific fragmentation occurs.

Further studies are needed to understand the mechanism of nanophotonic interactions through studying NAPA with modified geometries and material parameters. We intend to explore the effect of nanopost shape and electrical conductivity on ion yields. Detailed optical characterization will also be conducted using spectroscopic reflectometry, polarization dependent reflectivity and UV-VIS spectroscopy of the NAPA.

Figures

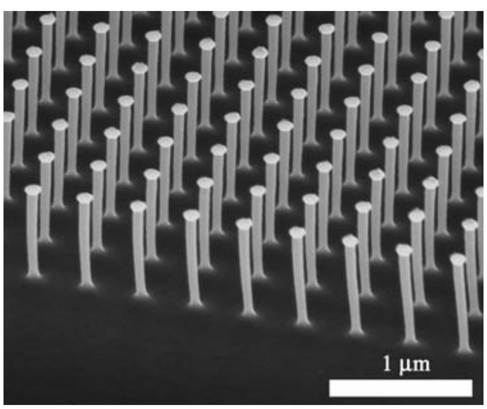

Figure 1. SEM image of NAPA with 1000 nm post height, 100 nm post diameter, and 350 nm periodicity.

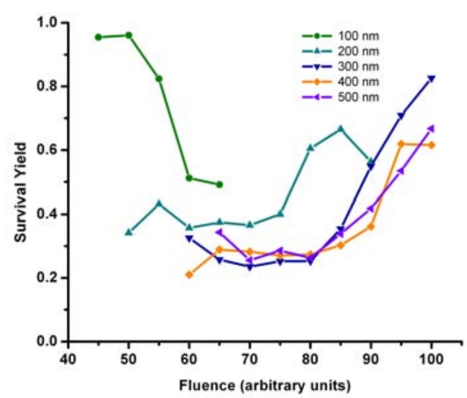

Figure 2. Survival yields of 4methyl-benzylpyridinium ions desorbed from NAPA of varying diameters and a post height of 1000 nm.

References

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(2) Walker, B. N.; Razunguzwa, T.; Powell, M.; Knochenmuss, R.; Vertes, A. *Angewandte Chemie-International Edition* **2009**, *48*, 1669-1672.